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The pre-atmospheric hydrogen inventory of CM carbonaceous chondrites

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Abstract

Understanding the quantity and isotopic composition of water that has been delivered to Earth over its history is crucial for models our planet's evolution, and predicting habitability across the solar system. Here we have used stepwise pyrolysis to measure the hydrogen inventory of CM carbonaceous chondrites, which are likely to have been a major source of volatiles for the early Earth. Stepwise pyrolysis potentially enables the carriers of pre-terrestrial hydrogen to be identified, and distinguished from hydrogen that may have been added during the meteorite's time on Earth. Twelve CM meteorites were analysed, and from their bulk hydrogen composition, petrologic type and nature of parent body processing, they can be divided into three subsets. The CMs of subset A have been mildly aqueously altered. Their hydrogen is hosted by isotopically light phyllosilicate, isotopically heavy organic matter, and adsorbed terrestrial water that is comparable to or slightly heavier than phyllosilicate. The subset B meteorites have been heavily aqueously altered and their hydrogen is also in phyllosilicate, organic matter and adsorbed terrestrial water. Their pyrolysis profiles differ from subset A in that the phyllosilicates dehydroxylate at higher temperatures owing to differences in mineralogy and chemical composition. The hydrogen that was evolved from organic matter may also have been isotopically lighter owing to loss of deuterium during aqueous alteration. Subset C meteorites were heated on their parent body after aqueous alteration, leading to loss of hydrogen from phyllosilicates and organic matter such that half of the water that they evolve was added after falling to Earth. Taking the 12 CMs together, an average of 0.20 wt.% H (21 % of total H) is terrestrial, and recalculation of bulk compositions without this component can raise bulk δD of individual meteorites by up to 73‰. Carbonaceous chondrites in our collections differ in the abundance and isotopic composition of hydrogen relative to their parent asteroid(s). An accurate understanding of the nature of water that was delivered to early Earth can only come from the analysis of materials that have been isolated from the terrestrial atmosphere, such as those returned from Ryugu and Bennu.

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Keywords: Carbonaceous chondrite; Hydrogen; Phyllosilicate; Organic matter; Contamination

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1. INTRODUCTION

C-complex asteroids formed within the protoplanetary disk by accretion of anhydrous minerals (silicates, sulphides and metal), organic matter and ices. They are spectrally similar to carbonaceous chondrite meteorites and so are likely to be their parent bodies (Chapman et al., 1975; Gradie and Tedesco, 1982; Bates et al., 2019). The heliocentric distance at which the C-complex asteroids formed is debated, although the deuterium/hydrogen (D/H) ratio of water in carbonaceous chondrite meteorites (CMs and CIs) suggests that they accreted at ~3–7 AU (Alexander, 2017). These meteorites are believed to have delivered asteroidal water to the terrestrial planets early in their history, along with other volatiles including carbon (Marty 2012; Alexander et al., 2012, 2018; Alexander, 2017). A good understanding of the chemical and isotopic composition of the materials that were accreted to make C-complex asteroids, and that were also formed by their subsequent aqueous and thermal alteration, is therefore essential in order to be able to model the transfer of volatiles throughout the early solar system.

Here we have analysed the Mighei-like (CM) carbonaceous chondrites in order to investigate the H content and isotopic composition of their parent C-complex asteroid (s). The CMs contain ~10 wt.% structural water (H_2O^+; Jarosewich, 1990) with an average D/H ratio of $148 \pm 20 \times 10^{-6}$ (1σ), which corresponds to a δD of -53 ± 130‰ ($\delta D = (D/H_{sample}/D/H_{standard\ (VSMOW)} - 1) \times 1000$, where VSMOW denotes Vienna Standard Mean Ocean Water with a D/H ratio of 155.76×10^{-6}) (Lécuyer et al., 1998; Alexander, 2017). Two principal carriers of H have been identified in the CMs: hydrous silicates (principally phyllosilicates) and organic matter (Boato, 1954; Kolodny et al., 1980; Robert and Epstein, 1982; Eiler and Kitchen, 2004). Phyllosilicates were formed by parent body aqueous alteration (Dufresne and Anders, 1962; McSween 1979a, b; Bunch and Chang 1980). They host most of the H in these meteorites, and are isotopically light (δD −200 to −450‰; Alexander et al., 2012). Piani et al. (2018) identified a second hydrated silicate in the least altered lithology of the CM Paris ($\delta D > -69 \pm 163$‰) that is probably amorphous material whose H was acquired at heliocentric distances of greater than 7 AU. Organic matter was also accreted from the nebula and is isotopically heavy (δD ~ 3500‰) (Kolodny et al. 1980; Robert and Epstein 1982; Alexander et al. 2007). Whilst hydrated silicates and organic matter will be the principal determinants of the abundance and isotopic composition of H in the CMs, all meteorites have adsorbed water from Earth's atmosphere (e.g., Kolodny et al. 1980; Jarosewich, 1990; Eiler and Kitchen 2004; Vacher et al. 2020). Additionally, CM finds, and falls that have been on Earth for more than a few decades, can contain terrestrially formed hydrous minerals such as goethite, ferrihydrite, gypsum, and clay minerals; terrestrial H can also be added by exchange with OH in the phyllosilicates (e.g., Lee 1993; Velbel 1988; Bland et al., 1998, Lee and Bland, 2004; Gounelle and Zolensky, 2001; Rubin et al., 2007; Lee et al., 2021). The H isotopic composition of this terrestrial water (δD ~ 50 to −400‰; Lécuyer et al., 1998) will be equal to or heavier than that of the pre-terrestrial phyllosilicates.

Two questions need to be answered in order to help predict the volume and isotopic composition of water that was delivered to the terrestrial planets by CM carbonaceous chondrites: (i) are those meteorites that fall to Earth at the present-day chemically and isotopically equivalent to primordial CMs? and (ii) have the CMs in our collections been chemically and isotopically contaminated during their time on Earth? In answer to the first question, it is reasonable to assume that the parent bodies of primordial CMs accreted in a similar part of the protoplanetary disc to the parent bodies of present-day CMs, and so acquired comparable amounts of D-rich organic matter. The timing and extent of aqueous alteration to form the phyllosilicates would have had a major effect on the bulk H content and isotopic composition of the primordial CMs. As aqueous alteration took place very early ($4563.9^{+0.6}_{-0.7}$ Ma; Fujiya et al., 2012), the parent bodies are highly likely to have contained phyllosilicates. However, the amount of phyllosilicate-hosted H in any one meteorite depends on the degree of aqueous alteration of the parent body and also whether it had undergone post-hydration heating. Such thermal alteration would have significantly reduced H abundance, but the timing of post-hydration heating is debated, and it may not have affected those CMs that were accreted to early Earth (Amsellem et al. 2020). Overall therefore, present-day CMs are likely to be compositionally comparable to their primordial counterparts. An answer to the second question about whether or how CM meteorites have been altered once they have fallen to Earth requires accurate quantification of the amount and isotopic composition of terrestrial H that they contain.

Here we have sought to explore the effects of parent body processing and terrestrial contamination on the abundance and isotopic composition of H in a suite of CMs using stepwise pyrolysis. This technique has been successfully applied to the CMs previously (Kolodny et al. 1980; Robert and Epstein 1982; Eiler and Kitchen 2004), and was used here because it can potentially identify and distinguish between: (i) H that is hosted by phyllosilicate (strongly bound and isotopically light); (ii) H within organic matter (strongly bound and isotopically heavy); (iii) H that has been adsorbed from Earth's atmosphere (weakly bound and with a terrestrial isotopic composition). From a quantitative understanding of the abundance and isotopic composition of H that is hosted by these three components, the composition of meteorites prior to their atmospheric exposure can be better constrained, as can the quantity and isotopic composition of water that was accreted by early Earth.

2. MATERIALS AND METHODS

2.1. Meteorites analysed

Twelve CMs comprising one fall and 11 Antarctic finds were analysed (Table 1). Polished thin sections or blocks of all samples were characterised by backscattered electron imaging (BSE) at the University of Glasgow using a Zeiss

Table 1
The meteorites studied.

Meteorite	Fall or find/location/year	Weathering grade	Petrologic (sub)type		
			Rubin et al. (2007)	Alexander et al. (2013)	Howard et al. (2015)
Allan Hills (ALH) 83100	Find/Antarctica/1983	Be	2.1[1]	1.1	1.2[5]
Cold Bokkeveld	Fall/South Africa/1838	n/a	2.2	1.3	1.4
D'Angelo Bluff (DNG) 06004	Find/Antarctica/2006	B	———	1.8	1.7
Dominion Range (DOM) 08013	Find/Antarctica/2008	B/C	———	1.8	1.5
Elephant Morraine (EET) 96029	Find/Antarctica/1996	A/B	———	2.0[3] (H)	———[6]
LaPaz Icefield (LAP) 02239	Find/Antarctica/2002	B	———	1.7	1.5[7]
Lewis Cliff (LEW) 85311	Find/Antarctica/1985	Be	2.6–2.7[2]	1.9	1.7[8]
MacKay Glacier (MCY) 05230	Find/Antarctica/2005	B	———	1.8	———
Meteorite Hills (MET) 01075	Find/Antarctica/2001	B	———	1.5 (H)	1.3[9]
Pecora Escarpment (PCA) 91084	Find/Antarctica/1991	Be	———	1.8 (H?)	———
Queen Alexandra Range (QUE) 97990	Find/Antarctica/1997	Be	2.6	1.7	1.6
Scott Glacier (SCO) 06043	Find/Antarctica/2006	B/Ce	———	1.15[4]	1.2

——— not determined
H denotes classified as "Heated"
H? denotes classified as "Heated?"
[1] de Leuw et al. (2010).
[2] Tentitatively classified by Choe et al. (2010).
[3] Calculated from data inAlexander et al. (2012)
[4] An average of two analyses.
[5] Lindgren et al. (2020).
[6] PS-XRD data in Lee et al. (2016) show that the phyllosilicates have been amorphised by heating.
[7] Data from LAP 02333 with which it is paired.
[8] Lee et al. (2019b).
[9] Lee et al. (2019a).

Sigma SEM operated at 20 kV (Fig. 1). The petrologic type of the 12 CMs has been previously determined by Alexander et al. (2013) using the amount of H in the water/OH of bulk samples. In this classification scheme a petrologic type 3 refers to a nominally anhydrous CM, and type 1 to a meteorite ideally containing ~1.44 wt.% H (i.e., equal to stoichiometric Mg-serpentine). To date no type 3 CMs have been described. Nine of the studied meteorites have also been classified by Howard et al. (2015) using their phyllosilicate fraction (PF) as measured by X-ray diffraction (XRD). PF is the volume of total phyllosilicate divided by total phyllosilicate plus anhydrous silicate. Petrologic type 3 has a PF of < 0.05 and type 1 > 0.95. The petrologic subtypes of four of the CMs were also determined by Rubin et al. (2007), and are consistent with classifications by Alexander et al. (2013) and Howard et al. (2015) (Table 1).

2.1.1. Degree of aqueous alteration and post-hydration heating

Nine of the 12 meteorites have been aqueously altered but have not undergone detectable post-hydration heating: Allan Hills (ALH) 83100, Cold Bokkeveld, Scott Glacier (SCO) 06043, D'Angelo Bluff (DNG) 06004 (Fig. 1a), Dominion Range (DOM) 08013, LaPaz Icefield (LAP) 02239, Lewis Cliff (LEW) 85311, MacKay Glacier (MCY) 05230, Queen Alexandra Range (QUE) 97990 (Table 1). Together, these nine meteorites span most of the range in petrologic (sub)types of the CMs (Table 1). Two of the studied meteorites, Elephant Morraine (EET) 96029 and Pecora Escarpment (PCA) 91084, were classified by Alexander et al. (2012, 2013) as "Heated" and "Heated?", respectively, because they have a lower wt.% H than CMs of a similar δD (Table 1). The classification of EET 96029 was confirmed by Lee et al. (2016), who presented petrographic, mineralogical and isotopic evidence that it had been heated to ~400–600 °C after aqueous alteration. Although PCA 91084 was described as "Heated?" by Alexander et al. (2012, 2013), SEM images show that its matrix has the fractured appearance that is characteristic of CMs that have experienced significant dehydroxylation accompanying post-hydration heating (Lindgren et al., 2020) (Fig. 1b). As this meteorite is unusually carbonate-poor (0.02 wt.% carbonate hosted C, Alexander et al. 2015), PCA 91084 is likely to have been heated to above the calcination temperature of carbonates (>~700 °C; Lindgren et al. 2020). The twelfth meteorite, MET 01075, was also classified by Alexander et al. (2013) as "Heated" given the low wt.% H for its δD. However, the sample of MET 01075 that was studied by Lee et al. (2019a) contained tochilinite and crystalline phyllosilicates and so had not been heated above ~300–400 °C. Whilst results from these two studies of MET 01075 are contradictory, they can be reconciled if MET 01075 is a breccia and the subsamples analysed had experienced different post-hydration histories. Nonetheless, Lee et al. (2019a) found that another subsample of MET 01075 contains sodalite that formed by alkali-halogen metasomatism prior to aqueous alteration, further suggesting that at least some parts of this meteorite had experienced a different thermal history to the other 11 CMs. The sample set therefore comprises nine CMs that have been aqueously altered to different degrees, two that have undergone post-hydration heating, and one with evidence for multiphase heating and metasomatic alteration.

2.2. Stepwise pyrolysis

This study used 33–79 mg chips from meteorite interiors. Chips were employed in preference to powders in an attempt to minimize terrestrial contamination, and also so that the analysed fragments could be made into polished thin sections for subsequent SEM work. Prior to analysis, the samples had been held in Perspex containers, apart for MET 01075b that was stored in a desiccator. The procedure for stepwise pyrolysis used here has been previously applied to meteorite samples (Lee et al. 2018). Each chip was placed in an all-glass vacuum line, which was pumped down overnight. Samples were incrementally heated via a temperature-controlled resistance furnace (25–700 °C) and a temperature-controlled induction furnace (>700 °C) over

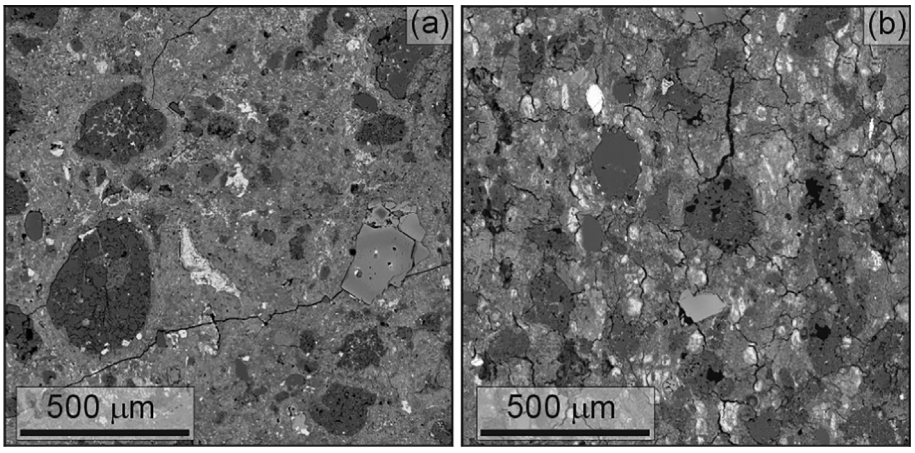

Fig. 1. BSE images of DNG 06004 (a) and PCA 91084 (b). Both meteorites contain chondrules and silicate mineral grains in a fine-grained matrix, and both have a petrologic type of 1.8 (Table 1). Unlike DNG 06004, PCA 91084 has experienced post-hydration heating leading to dehydroxylation of phyllosilicates and fracturing of the fine-grained matrix.

seven steps: 25–100, 100–200, 200–300, 300–400, 400–500, 500–700 and 700–1000/1100 °C (±5 °C). They were held at each temperature for a minimum of 30 minutes. The gases released were first stored in a cold trap at −196 °C using a liquid N_2 bath, which was then replaced by a mixture of dry ice and acetone at −78 °C, trapping water but releasing other gases. The yield of gas that was not trapped at −78 °C was measured using an Edwards PR10-C Pirani vacuum pressure gauge. The dry ice and acetone bath was then removed from the cold trap, gently heated, and the water released. This water was reduced to H_2 by exposure to Cr powder at 850 °C (Donnelly et al. 2001). The yield of H in each step was measured using the Pirani vacuum pressure gauge, and the H_2 was collected using a mercury Toepler pump into a small borosilicate vessel with Teflon-sealed high-vacuum valves. The vessels were taken immediately to a VGI Optima mass spectrometer for H isotope measurement. In-run repeat analyses of water standards (international standards GISP, V-SMOW and internal standard LT-STD) gave a reproducibility of better than ± 2‰ for δD.

Results are listed in the Electronic annex as the yield of H_2 in μmol/mg at each step, the corresponding wt.% H and H_2O, and the H isotopic composition expressed as δD. Steps yielding < 0.15 μmol/mg were added to the subsequent aliquot for isotopic analysis. Bulk H is the sum of H evolved in all steps, and bulk δD is the isotopic composition of H evolved at each step added as a proportion of total H. Eleven of the 12 meteorites were analysed once whereas two samples of MET 01075 were analysed (referred to as MET 01075a and b). Results from both of the MET 01075 samples are in the Electronic annex and show good reproducibility (bulk H = 0.91 wt.% for both, and δD differs by 20‰). In the text, figures and tables an average of the two analyses is quoted, and referred to as MET 01075c.

3. RESULTS

3.1. Bulk compositions

The abundance and isotopic composition of H in the 12 CMs is plotted in Fig. 2. The nine CMs that were not heated after aqueous alteration fall into two subsets (A and B) (Fig. 2). Subset A comprises six meteorites (DNG 06004, DOM 08013, LAP 02239, LEW 85311, MCY 05230, QUE 97990) whose wt.% H correlates well with δD ($R^2 = 0.82$). The three other CMs that comprise subset B (ALH 83100, Cold Bokkeveld, SCO 06043) differ from subset A in bulk δD, and in a lack of a correlation between wt.% H and δD (Fig. 2). As regards the two CMs that have undergone post-hydration heating, PCA 91084 plots within subset A whereas EET 96029 is separate from both subsets. As they have a similar bulk δD despite the difference in wt. % H, these two meteorites are allocated to subset C. MET 01075c is described and discussed separately because it is compositionally different to the other heated meteorites of subset C (Fig. 2). The petrologic types of the 12 CMs correlate well with both wt.% H and δD (Tables 1 and 2, Fig. 3). The correlation of petrologic type with wt.% H is stronger using the classification of Alexander et al. (2013) whereas δD correlates better with petrologic type as determined by Howard et al. (2015).

3.2. Stepwise profiles

The profile of each sample is in the Electronic annex, and results are described here in the context of the three

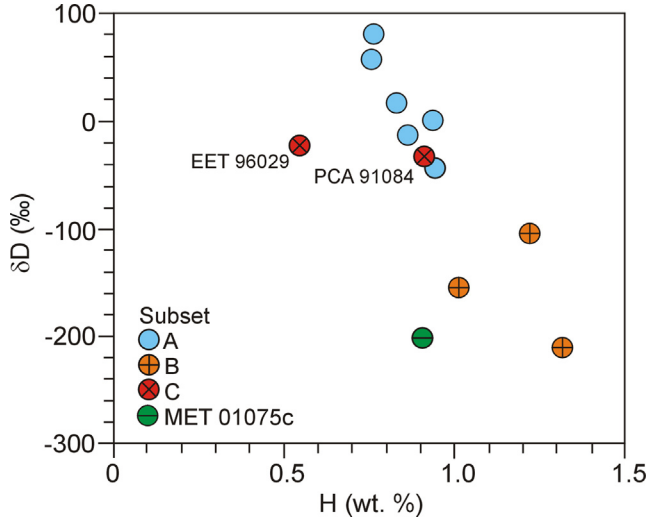

Fig. 2. Bulk hydrogen compositions of the 12 CMs analysed. The two subset C samples are labelled.

Table 2
Bulk compositions of the meteorites studied.

Subset	Meteorite	Bulk C (wt.%)[1]	Bulk H (wt.%)[1]	Bulk δD (‰)[1]	Bulk C/H[1]	Bulk H (wt.%)	Bulk δD (‰)	Bulk C/H
A	DNG 06004	2.04	0.99	−3	2.07	0.94	0	2.17
A	DOM 08013	1.92	0.96	47	2.00	0.76	57	2.53
A	LAP 02239	1.91	1.02	−36	1.87	0.95	−43	2.01
A	LEW 85311	2.03	0.91	119	2.23	0.77	80	2.64
A	MCY 05230	2.00	0.98	−18	2.03	0.87	−13	2.30
A	QUE 97990	2.00	1.04	–22	1.91	0.84	16	2.38
B	ALH 83100	1.90	1.46	−201	1.30	1.02	−154	1.86
B	Cold Bokkeveld	2.45	1.35	−168	1.81	1.23	−104	1.99
B	SCO 06043	1.34	1.36	–223	0.98	1.32	−210	1.02
C	EET 96029	1.51	0.81	−85	1.86	0.55	−21	2.75
C	PCA 91084	1.58	0.93	−75	1.69	0.92	−31	1.72
	MET 01075c	1.59	1.12	−184	1.43	0.91	−211	1.75
		Bulk-1 H (wt.%)	Bulk-1 δD (‰)	Bulk-1 C/H	Bulk-2 H (wt.%)	Bulk-2 δD (‰)	Bulk-2 C/H	
A	DNG 06004	0.91	2	2.24	0.78	14	2.62	
A	DOM 08013	0.69	74	2.78	0.51	130	3.76	
A	LAP 02239	0.90	−41	2.12	0.8	−36	2.39	
A	LEW 85311	0.69	99	2.94	0.55	143	3.69	
A	MCY 05230	0.84	−10	2.38	0.77	−4	2.60	
A	QUE 97990	0.77	22	2.60	0.61	41	3.13	
B	ALH 83100	1.01	−155	1.88	0.98	−156	1.94	
B	Cold Bokkeveld	1.20	−105	2.04	1.01	−114	2.43	
B	SCO 06043	1.26	−216	1.06	1.04	−236	1.29	
C	EET 96029	0.47	−19	3.21	0.30	−1	5.03	
C	PCA 91084	0.82	–23	1.93	0.48	−2	3.29	
	MET 01075c	0.91	−211	1.75	0.87	−216	1.83	

[1] Data from Alexander et al. (2012). All C/H values are calculated using C data in Alexander et al. (2012). Two analyses of SCO 06043 are averaged. All other data are from the present study.

subsets (Fig. 4). The proportion of total H that was evolved from subset A samples increases in each step to 300–400 °C, then falls at higher temperatures. Average δD varies little in the first three steps then becomes significantly heavier (Fig. 4a, b). As regards the three CMs of subset B, the proportion of total H rises in each of the first six steps to reach a peak at 500–700 °C, then falls in the highest temperature step. δD becomes progressively lighter over all seven steps and correlates well with temperature ($R^2 = 0.94$) (Fig. 4c, d). The two CMs of subset C show no clear pattern in the proportion of total H that is evolved with temperature. δD varies over a fairly narrow range (−70 to 34‰); it gets heavier in the first six steps and correlates well with temperature ($R^2 = 0.98$) (Fig. 4e, f). The step heating profiles for MET 01075a and MET 01075b are similar to the subset B meteorites although differ in the high proportion of H that is evolved in the 500–700 °C step (57 % and 51 % of total H, respectively; Electronic annex).

4. DISCUSSION

Here we first consider the various hosts of H and their abundance in the CMs analysed, and evaluate the reasons for differences in the amount and isotopic composition of H between meteorites. We then compare and contrast these results with findings from previous studies of H in the CMs, and finally consider the implications of our work for understanding the delivery of H to early Earth.

4.1. Carriers of H in the CMs

The principal H-bearing constituents of the CMs are phyllosilicates, tochilinite, gypsum, Fe-oxyhydroxides, organic matter, and adsorbed molecular water (Lee 1993; McSween 1979a, b; Bunch and Chang 1980; Tomeoka and Buseck, 1985; Zolensky et al., 1993; Rubin et al. 2007; Alexander et al. 2012, 2013; Howard et al., 2015). Hydrogen is also contained within nominally anhydrous minerals (e.g., olivine, pyroxene), but given its low concentration (up to ~1000 ppm H_2O; Stephant et al., 2017) and the stability of olivine and pyroxene during stepwise pyrolysis, these phases are not considered further.

Organic matter was accreted from the solar nebula and is isotopically heavy (possibly as high as δD ~ 3500‰ for insoluble organic matter; Alexander et al. 2007, 2012). The abundance of organic matter in the CMs can be estimated from the amount of C in bulk samples (~1–3 wt.% C; Alexander et al. 2012), although carbonates also make a contribution (0.03–0.60 wt.%; carbonate-hosted C; Alexander et al. 2015). Assuming that organic matter has a C/H ratio of 18 by weight (Alexander et al. 2013), it will contribute ~0.06–0.17 wt.% H to a bulk CM. All of the other carriers of H were formed by water–rock interaction

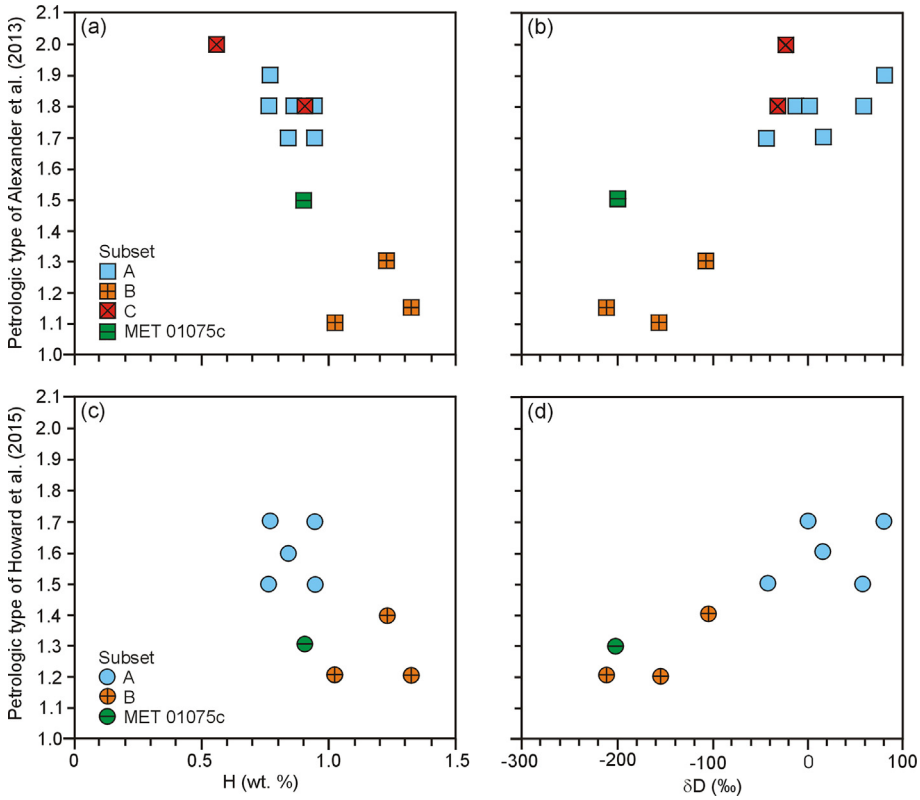

Fig. 3. Petrologic type of the analysed CMs plotted against their wt.% H and δD. The petrologic type of all 12 samples was determined by Alexander et al. (2013), and correlates well with wt.% H ($R^2 = 0.70$) (a) and δD ($R^2 = 0.68$) (b). The petrologic type of nine of the CMs was determined by Howard et al. (2015) and correlates poorly with wt.% H ($R^2 = 0.41$) (c) although well with δD ($R^2 = 0.80$) (d). Regression lines are not shown.

within the parent body or on Earth. Phyllosilicates comprise 56–88 vol. % of the CMs (Howard et al., 2015) and are isotopically light (δD −200 to −450‰; Alexander et al. 2012). They can be divided into Mg,Fe serpentine, which is relatively H-rich (~1.4 wt.% H for chrysotile), and cronstedtite with a lower abundance (~1 wt.% H). Phyllosilicates will therefore contribute a minimum of 0.6 wt.% and maxiumum of 1.2 wt.% H to a bulk analysis depending on the relative volumes of Mg,Fe serpentine and cronstedtite. Tochilinite contains ~0.2 wt.% H. It formed by parent body aqueous alteration (Tomeoka and Buseck, 1985; Palmer and Lauretta 2011) and comprises up to ~3–4 vol. % of a CM (Howard et al. 2015). This mineral therefore accounts for a maximum of 0.01 wt % H of a bulk CM.

Gypsum and Fe-oxyhydroxides are relatively H-rich (gypsum = 2.3 wt.% H; goethite and ferrihydrite = 1.1 and ~0.6 wt.% H, respectively) and may occur in many CMs although in low abundance (Lee 1993; Airieau et al. 2005; Rubin et al., 2007). As these minerals are likely to have formed on Earth, they will have a terrestrial isotopic composition. Terrestrial water can also be absorbed from the atmosphere, and is a significant source of H in the CMs. For example, Jarosewich (1990) measured the structural water (H_2O^+) and hydration water (H_2O^-) of six CMs (ALH 83100, ALH 83102, Banten, Murchison, Yamato (Y)-791824, Y-793321). The H_2O^- was quantified from weight loss at 110 °C. Of the 9.2–13.4 wt.% H_2O (1.0–1.5 wt.% H) that these meteorites contain, H_2O^+ comprises 6.5–12.1 wt.% (0.7–1.4 wt.% H) and H_2O^- 1.1–2.7 wt.% (0.1–0.3 wt.% H). Therefore, a significant proportion of the total H of these CMs had been adsorbed from Earth's atmosphere. The amount and isotopic composition of the adsorbed component has been quantified in the present study, and is discussed below.

4.2. Abundance of the various carriers

4.2.1. Phyllosilicate and organic matter

The correlation between wt.% H and δD in subsets A and B when taken together (Fig. 2) is consistent with the H budget of these nine samples being determined predominantly by the relative proportions of low H/high δD organic matter and high H/low δD phyllosilicate. Thus, as subset A samples are isotopically heavier than subset B, they should have a higher ratio of organic matter to phyllosilicate. This inference is supported by bulk C/H data showing that meteorites of subset A have a higher C/H ratio than subset B (2.01–2.64 versus 1.02–1.99, respectively) and a correspondingly heavier bulk δD (−43 to 80‰ versus −210 to −104‰, respectively) (Table 2, Fig. 5a). These conclusions agree with findings from previous H and C measurements of CMs (Eiler and Kitchen, 2004; Alexander et al., 2012, 2013). As discussed in Section 4.3, all of the samples that were analysed in the present

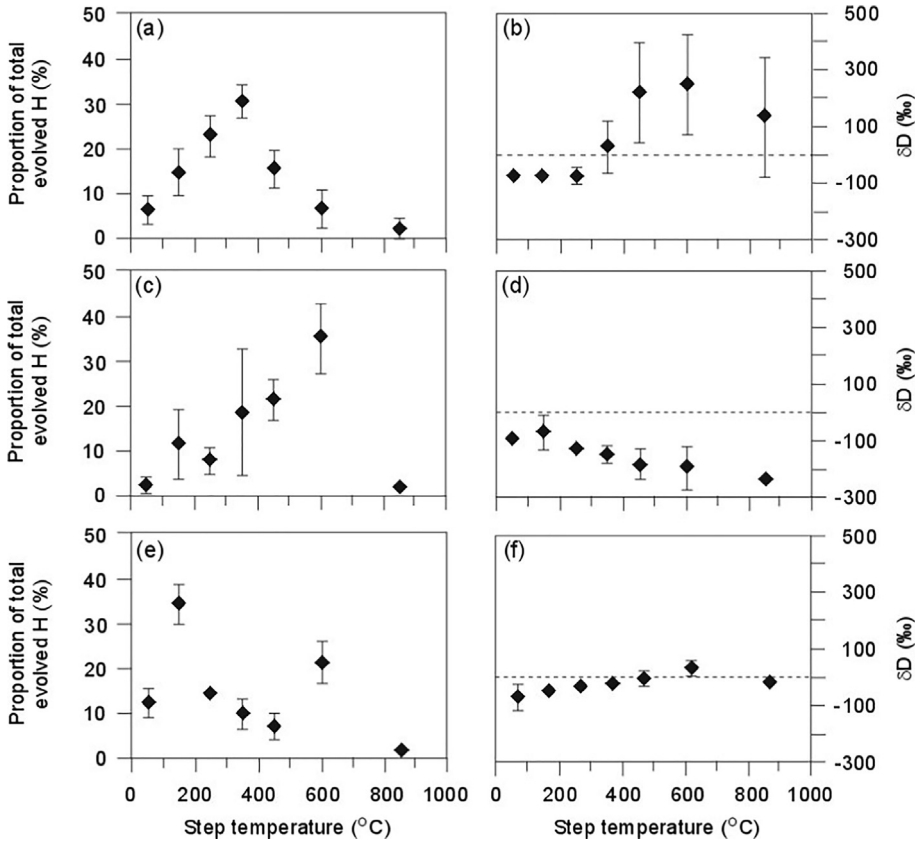

Fig. 4. Stepwise pyrolysis results for the six meteorites of subset A (a, b), three of subset B (c, d) and two of subset C (e, f). Plotted for each subset is the proportion of total H that was evolved in each temperature step, and its isotopic composition (datapoints are averages of the analysed samples, and error bars are 1σ). Datapoints are positioned in the middle of the temperature range of each step. Some samples were heated to 1000 °C, whereas others were heated to 1100 °C but are plotted as 1000 °C for comparability. The dashed lines in (b), (d) and (f) denote 0‰.

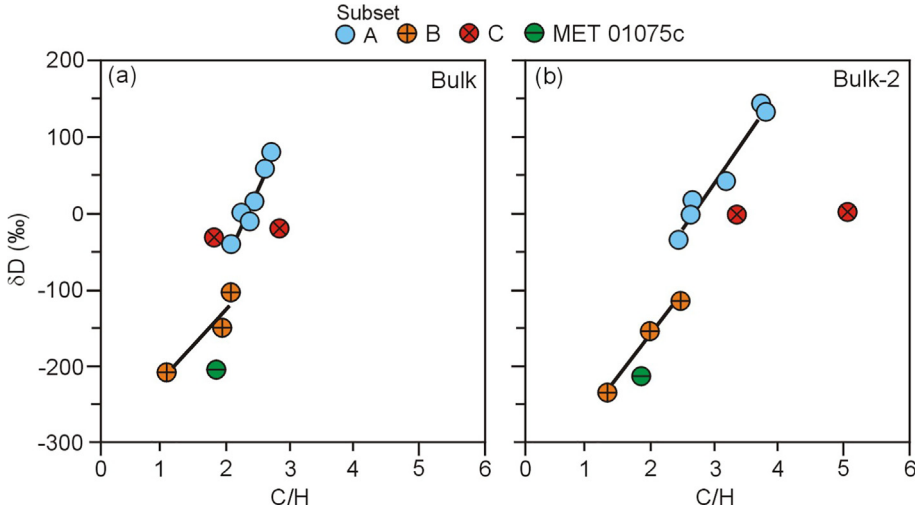

Fig. 5. The bulk C/H ratio (wt.%) of the 12 CMs plotted against bulk δD. The wt.% H and δD data are from the present study whereas wt.% C for each meteorite is taken from Alexander et al. (2012) (an average of their two analyses of SCO 06043 was used) (Table 2). (a) C/H and δD calculated using H that was evolved over all of the pyrolysis steps. Regression lines are plotted for subsets A and B ($R^2 = 0.92$ and 0.87, respectively). (b) C/H and δD calculated without H that was evolved below 200 °C, which is assumed to be an adsorbed terrestrial component (termed bulk-2). Regression lines are plotted for subsets A and B ($R^2 = 0.97$ and 0.99, respectively).

study contain adsorbed terrestrial water. Recalculating C/H and δD without this component (described in the following sections as bulk-2) increases the correlation coefficients of subsets A and B, and the regression lines for the two datasets become parallel (Fig. 5b). This result further supports the conclusion that the main controls of the pre-terrestrial H inventory of the CMs are phyllosilicate and organic matter.

Isotopically heavy H from organic matter is most evident in the higher temperature pyrolysis steps of the subset A samples (Fig. 4b). However, this high δD component cannot be identified in the pyrolysis profiles of subsets B and C (Fig. 4d, f), and MET 01075a & b (Electronic annex). A lack of organic matter cannot be the sole reason for this difference because all samples have a similar wt.% C (Table 2). One reason for the apparent lack of isotopically heavy H in subset B and MET 01075a & b is that it was diluted by isotopically light H, which as described below was evolved from the phyllosilicates at higher temperatures than in subset A. Another possible explanation is that D was lost from organics as they reacted with liquid water during the extensive aqueous alteration of subset B and MET 01075; this process has been proposed by Alexander et al. (2007). Thus, aqueous alteration accounts for the correlation between petrologic type and both wt.% H and δD for subsets A and B; with progressive alteration the ratio of high H/low δD phyllosilicate to low H/high δD organic matter increases, isotopically heavy H from organic matter is diluted, and D may also be lost from organic matter (Fig. 3, Table 2). If the latter process was operative, the distinct differences in bulk δD and pyrolysis profiles between subsets A and B show that D was more readily lost from organic matter beyond a threshold degree of aqueous alteration, which corresponds to a petrologic type of 1.5 (Howard et al. 2015) and 1.7 (Alexander et al. 2013). The absence of isotopically heavy H from the pyrolysis profile of subset C is most likely due to degradation of organic matter during post-hydration heating (Remusat et al., 2009), which can particularly affect the more D-rich component (Alexander et al., 2007). Isotopic exchange between organic matter and water during aqueous alteration prior to heating can be discounted as a mechanism for loss of D from EET 96029 because is one of the least aqueously altered CMs yet described (Lee et al., 2016).

Stepwise pyrolysis profiles provide further insights into the abundance and isotopic composition of H that is hosted by phyllosilicate and organic matter (Fig. 4). The proportion of H released from subset A samples is greatest in the 300–400 °C step (average 31 % of total H, 1σ 3.8 %), which is interpreted to represent the peak of phyllosilicate dehydroxylation. This conclusion is also consistent with δD, which is relatively light up to 300–400 °C and becomes heavier at higher temperatures as organic matter makes a greater contribution (Fig. 4b). A 300–400 °C peak temperature for phyllosilicate dehydroxylation is lower than expected (e.g., ~400–770 °C; Garenne et al. 2014), although Akai (1992) and Lindgren et al. (2020) have found that dehydroxylation can begin below 400 °C. Subset B (plus MET 01075a & b) differs from subset A in that the largest release of H, again inferred to correspond to phyllosilicate dehydroxylation, is in the 500–700 °C step (average 35 % of total H, 1σ 7.9 %). The contrasts in peak dehydroxylation temperature between subsets A and B may reflect differences in phyllosilicate chemical composition and mineralogy because Mg,Fe serpentine dehydroxylates at higher temperatures than Fe-rich phyllosilicate (i.e., cronstedite) (King et al., 2015; Lindgren et al., 2020). Accordingly, Mg,Fe serpentine is more abundant than cronstedtite in subset B and MET 01075 (Table 3). However, if chemistry and mineralogy were the sole control of dehydroxylation temperature, Mg,Fe serpentine should be less abundant than cronstedtite in subset A, which is only true for two of the five meteorites (Table 3). Therefore, other factors may contribute to inter-meteorite and inter-subset differences in dehydroxylation temperature, for example crystal size or fine scale intergrowths (e.g., cronstedtite with tochilinite) (King et al., 2015).

MET 01075c has a low bulk wt.% H relative to subset B samples with a comparable δD (Fig. 2). Alexander et al. (2013) used similar findings to classify MET 01075 as "Heated", although the mineralogy of a subsample of this meteorite that was analysed by Lee et al. (2019a) is inconsistent with that classification. The stepwise pyrolysis profiles of MET 01075a & b show that their phyllosilicates evolve a larger proportion of H at 500–700 °C than any of the other 11 samples (Electronic annex). The distinctiveness of MET 01075 may be related to mineralogical and chemical alteration accompanying alkali-halogen metasomatism (Lee et al., 2019a).

4.2.2. Adsorbed terrestrial water

The two CMs of subset C have a similar bulk δD but differ in wt.% H (Fig. 2). A comparable pattern of a relatively wide range in bulk wt.% H but narrow range of δD was documented by Alexander et al. (2012, 2013) for CMs that had undergone post-hydration heating. The highest proportion of H that was evolved from the two subset C meteorites is in the 100–200 °C step, with an average δD of −71‰ (Fig. 4, Electronic annex). These properties are consistent with H being sourced from loosely bound molecular water, which is released from meteorites at < 200 °C (Garenne et al., 2014). Hydrogen that was evolved by subset C is considerably less variable in isotopic composition over the whole temperature range than was evolved by subsets A and B (Fig. 4f). This result suggests that much of the indigenous phyllosilicate- and organic matter-hosted H had been removed by parent body heating to leave adsorbed terrestrial water as a major source of H. The similarity in isotopic composition of water evolved in the first two steps of all 12 CMs indicates that the whole sample set is likely to contain adsorbed molecular water (Fig. 4). Average δD for the low temperature steps of the 12 samples is: 25–100 °C −75‰ (1σ 21‰), 100–200 °C −79‰ (1σ 23‰). The weighted average of the first two steps is δD −78‰ (1σ 21‰). The isotopic composition of this adsorbed component is much heavier than that of Antarctic ice (~−100 to −400‰ depending on location; Masson-Delmotte et al., 2008), which indicates that samples equilibrate rapidly once they have been moved to a new environment (i.e., from Antarctica to museums and laboratories, which for this study are

Table 3
Abundance of gypsum and phyllosilicate in the nine meteorites that have been analysed by XRD (vol. %).

Subset	Meteorite	Gypsum	Mg,Fe serpentine	Cronstedtite	Mg,Fe serpentine/cronstedtite	Total phyllosilicate
A	DNG 06004[1]	——	25.9	30.4	0.9	56.3
A	DOM 08013[1]	——	57.7	10.2	5.7	67.9
A	LAP 02239[1]	——	51.7	21.6	2.4	73.3
A	LEW 85311[2]	——	27.0	37.8	0.7	64.8
A	QUE 97990[1]	——	40.4	26.6	1.5	67.0
B	ALH 83100[1]	——	62.4	24.2	2.6	86.6
B	Cold Bokkeveld[1]	0.8	54.1	23.3	2.3	77.4
B	SCO 06043[1]	——	66.0	21.6	3.1	87.6
	MET 01075[3]	0.2	63.9	18.7	3.4	82.6

—— below detection limits.
[1] Howard et al. (2015).
[2] Lee et al. (2019b).
[3] Lee et al. (2019a).

in the northern hemisphere). This conclusion is supported by the small difference between the isotopic composition of water that was evolved at less than 200 °C from Cold Bokkeveld, the only fall analysed (δD −61‰), and the average of the whole sample set (δD −78‰).

4.3. Calculating pre-atmospheric compositions

Here we seek to quantify the effect of adsorbed terrestrial water on bulk compositions. As the amount and isotopic composition of H that is evolved at each temperature step was measured in the pyrolysis experiments, bulk compositions free of terrestrial H can potentially be calculated by removal of H that was evolved in the initial steps. Previous studies have recognized that terrestrial water is released at low temperatures. Jarosewich (1990) quantified it from the weight loss at 110 °C, whereas others have removed the terrestrial component prior to H analysis by preheating for a few hours or days to temperatures ranging from 120 °C (Vacher et al., 2020) to 180–200 °C (Boato 1954; Kolodny et al., 1980; Kerridge 1985). Heating to 200 °C should be sufficient to remove adsorbed molecular water (liberated at 25–200; Garenne et al., 2014) and will also dehydrate gypsum (95–170 °C; Strydom et al., 1995). However, there is evidence that terrestrial water could be more strongly bound. Eiler and Kitchen (2004) found that this component was evolved from CMs at ~250 °C, and any terrestrial Fe-oxyhydroxides will dehydroxylate at 200–400 °C (Garenne et al. 2014). Even more strongly bound terrestrial water could be present, for example within phyllosilicates that have formed by Antarctic weathering (Gooding, 1986; Lee and Bland, 2004) or even during museum curation (Bland et al. 2006). Note that not all of the water that is evolved at low temperatures will necessarily be terrestrial because tochilinite decomposes at ~245–300 °C (Fuchs et al., 1973; Tonui et al., 2014), and the CMs may contain gypsum that has formed by parent body aqueous alteration (Lee 1993; Airieau et al. 2005; Lee et al., 2021). Furthermore, weakly bound pre-terrestrial H could be present, although the isotopic composition of the first two steps (δD −78‰) neither proves or disproves that possibility.

In order to correct for adsorbed terrestrial water, bulk H and δD values are here calculated in four ways: (i) using H evolved in all steps (termed bulk); (ii) without H evolved in the 25–100 °C step (bulk-1); (iii) without H evolved in the 25–100 and 100–200 °C steps (bulk-2); (iv) without H evolved in the 25–100, 100–200 and 200–300 °C steps (bulk-3). The impact on average wt.% H for the 12 meteorites is: bulk = 0.92 wt.%; bulk-1 = 0.87 wt.% (6 % lower); bulk-2 = 0.73 wt.% (21 % lower); bulk-3 = 0.58 wt.% (37 % lower). Recalculating bulk values without the adsorbed water can significantly change δD. For the subset A samples, δD of bulk-2 is between 7 and 73‰ higher than bulk (average 32‰), whereas for subset B samples δD of bulk-2 is lower than bulk by between 2 and 26‰ (average 13‰) (Table 2).

All of the 12 CMs that were analysed in the present study host adsorbed terrestrial water, as evidenced by the low temperatures at which it is evolved and its isotopic composition (Fig. 4). Alexander et al. (2012) studied the same 12 CMs, samples of which had been ground to < 150 μm and stored for days to weeks in a desiccator at room temperature prior to analysis. The two datasets correlate well with regards to bulk δD, but bulk H abundances from the present study are lower relative to Alexander et al (2012) by 0.01–0.44 wt.% H (average 0.15 wt.%) (Table 2, Fig. 6). Storage of samples in the present study under vacuum prior to the pyrolysis experiments may account for part of this difference. Another explanation may be that the powdered samples used by Alexander et al. (2012) adsorbed more water than the chips that were analysed for the present study. Vacher et al. (2020) determined the bulk compositions of powders of nine CM samples, which were preheated to 120 °C for 48 hours before analysis. Four of these meteorites had also been analysed by Alexander et al. (2012). In common with the present study, results from Vacher et al. (2020) were lower in wt.% H but comparable in δD to the same meteorites in Alexander et al. (2012) (apart for LON 94101) (Fig. 6).

Despite the finding that samples analysed in the present study have a lower abundance of H than the same CMs as measured by Alexander et al. (2012), the yield of H from

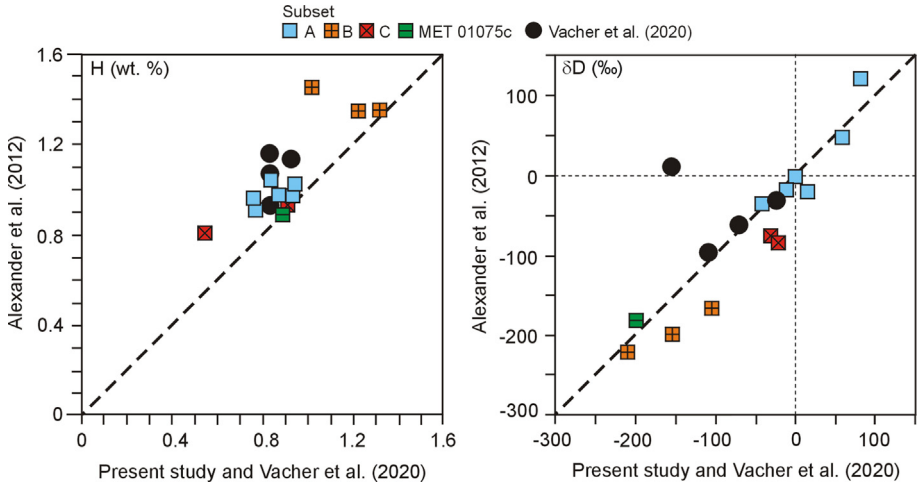

Fig. 6. Bulk wt.% H (left) and δD (right) of the 12 CMs that were analysed in the present study compared with the same meteorites as analysed by Alexander et al. (2012). Four of the CMs that were analysed by Vacher et al. (2020) (LON 94101, Mighei, Murchison, Murray) are likewise plotted against the same meteorites in Alexander et al. (2012). The vertical and horizontal dashed lines in the right hand plot denote 0‰.

low temperature pyrolysis steps indicates that they still have a significant quantity of adsorbed terrestrial water. Fig. 7a shows the impact of removal of this adsorbed terrestrial water on wt.% H and δD for the nine CMs of subsets A and B. Regression lines for bulk, bulk-1, and bulk-2 are approximately parallel to each other and to analyses of the same CMs by Alexander et al. (2012) but displaced to a lower wt.% H (Fig. 7a). Results from pre-heated samples in Vacher et al. (2020) are closest to the bulk-2 dataset in both wt.% H and the range of δD (Fig. 7b). Vacher et al. (2020) found that preheating to 120 °C removed ~10–30 % of the total H of a CM, whereas heating of the nine CMs of subset A and B to 200 °C removed 0.04–0.28 wt. % H (4–33 % of total H, average 20 %). These results are also in agreement with Jarosewich (1990), who measured 11–26 % hydration water (average 18 %) in five CMs that had not undergone post-hydration heating. The two samples of subset C lost 45 and 48 % of total H upon heating to 200 °C, which is consistent with 41 % hydration water measured by Jarosewich (1990) for the post-hydration heated meteorite Y-793321. Despite the good agreement in the amount of terrestrial water hosted by CMs between the present study, Jarosewich (1990) and Vacher et al. (2020), the samples analysed had been heated to different temperatures: 200 °C for the bulk-2 dataset in comparison to 110 °C and 120 °C for Jarosewich (1990) and Vacher

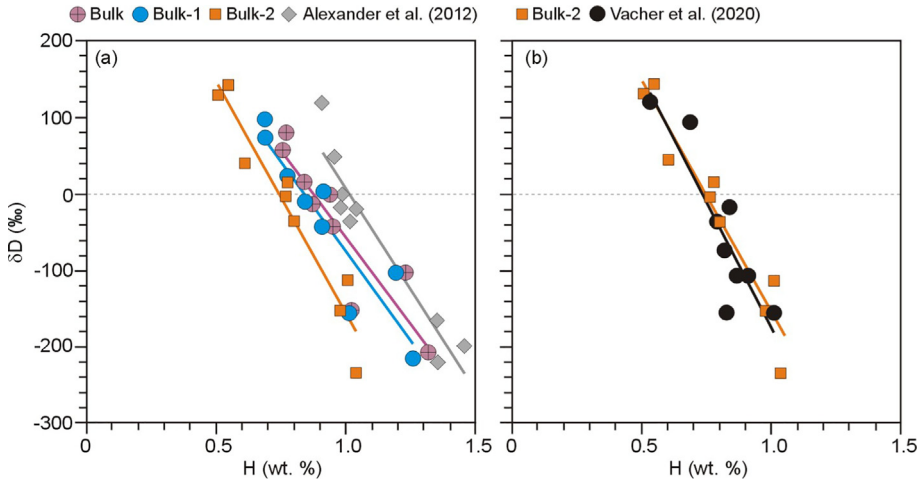

Fig. 7. Plots of wt.% H against δD. (a) The nine unheated CMs of subsets A and B. Compositions have been calculated using H measured over three different temperature ranges: bulk, bulk-1, and bulk-2. Correlation coefficients and equations of regression lines plotted for each dataset are: bulk (R^2 0.82, y = −451x + 394); bulk-1 (R^2 0.86, y = −470x + 396); bulk-2 (R^2 0.93, y = −614x + 457). Bulk compositions of the same meteorites in Alexander et al. (2012) are also plotted: R^2 0.91, y = −534x + 538. (b) Bulk-2 compositions of subset A and B samples together with the nine CM samples that were analysed by Vacher et al. (2020) after preheating to 120 °C (R^2 0.80, y = −656x + 483). The dashed lines in both graphs denote 0‰.

et al. (2020), respectively. This apparent contradiction may be explained by differences in sample preparation such that the loosely bound terrestrial water is lost at lower temperature from the powdered samples used by Jarosewich (1990) and Vacher et al. (2020) than from the chips that were analysed in the present study.

One way to test how close the bulk-2 values are to the H composition of CM lithologies before their exposure to the Earth's atmosphere could be to compare falls with finds; the latter may have adsorbed more water owing their longer terrestrial residence. Only one fall (Cold Bokkeveld) was analysed in the present study. It evolved 0.22 wt % H below 200 °C in comparison to 0.04–0.43 wt.% (average 0.19 wt. %) for the 11 finds. Thus there is no evidence for the fall having adsorbed less H, but this result is not unexpected because Cold Bokkeveld is the oldest CM fall (it fell in 1838) and could even have been exposed to liquid water before recovery (Lee et al. 2021). A fall that has been collected and analysed within hours or days may have less adsorbed water and so be closer to a pre-terrestrial H abundance and isotopic composition. However, true values for a CM lithology can only be obtained by the analysis of C-complex asteroids in-situ, or samples that have been returned, for example those from Ryugu and Bennu, and isolated from the Earth's atmosphere.

5. SUMMARY AND CONCLUSIONS

Stepwise pyrolysis has been successfully used to measure the abundance and isotopic composition of H in 12 CM carbonaceous chondrites. Results show that:

- The CMs have three principal carriers of H from three different sources: nebular organic matter, parent body phyllosilicate, and adsorbed terrestrial water. Other H-bearing minerals including gypsum, goethite and ferrihydrite may also occur, and could have formed by parent body and/or terrestrial alteration.
- Those meteorites that had been aqueously altered but had not undergone post-hydration heating (subsets A and B) evolve H from all three principal carriers. The isotopically heavy H from organic matter is most evident in pyrolysis profiles of the mildly aqueously altered meteorites (subset A). With higher degrees of aqueous alteration (subset B and MET 01075c) the high δD signature of organic matter is absent from stepwise profiles due to isotopic dilution by H from phyllosilicates and/or loss of D from the organics during aqueous alteration.
- Contrasts in temperatures of phyllosilicate dehydroxylation between mildly and highly aqueously altered CMs are partly due to differences in the heat resistance of cronstedtite and Mg,Fe serpentine.
- Heating of the nine samples of subsets A and B to 200 °C removed an average of 20 % of total H, most of which is assumed to be the adsorbed terrestrial component. Almost half of the H that was evolved from the post-hydration heated samples of subset C is terrestrial. Taking all 12 CMs together, an average of 21 % of total H (0.20 wt.% H) is the post-fall adsorbed component.
- Powdered CM samples that were pre-heated to 120 °C by Vacher et al. (2020) have a similar range of wt.% H and δD as chips that were heated to 200 °C in the present study. These compositions will be close to pre-atmospheric values, but how close cannot be determined by stepwise pyrolysis.
- Correction for terrestrial contamination is essential for accurately calculating the amount and isotopic composition H that CM meteorites, and probably also the CIs, could have delivered to early Earth.
- Samples returned from Ryugu and Bennu can provide pre-atmospheric compositions of C-complex asteroids as long as they are treated with scrupulous care to avoid any contact with the Earth's atmosphere.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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APPENDIX A. SUPPLEMENTARY DATA

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